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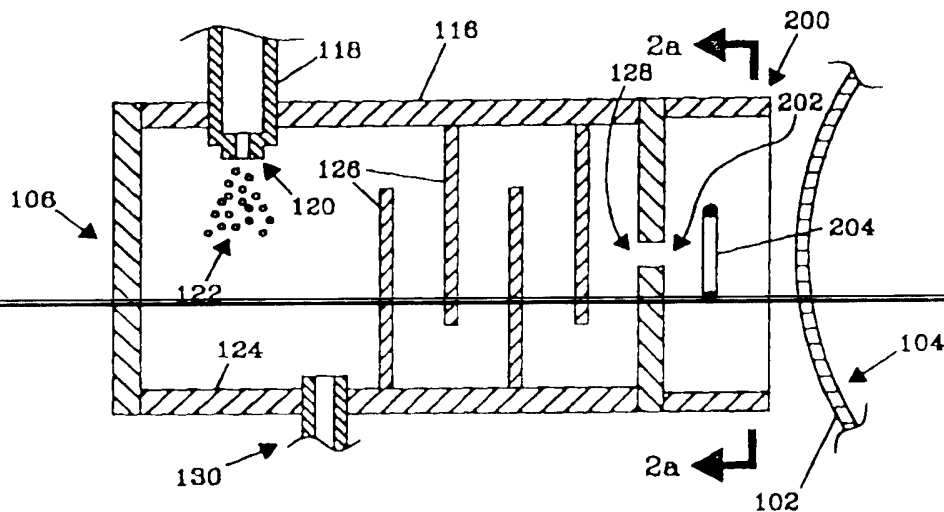
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(21) International Application Number: PCT/US98/20741 (22) International Filing Date: 29 September 1998 (29.09.98) (30) Priority Data: 08/939,594 29 September 1997 (29.09.97) US (71) Applicant: BATTELLE MEMORIAL INSTITUTE (US/US); Pacific Northwest Division, Intellectual Property Services, P.O. Box 999, Richland, WA 99352 (US). (72) Inventor: AFFINITO, John, D.; 2713 Kyle Road, Kennewick, WA 99338 (US). (74) Agent: ZIMMERMAN, Paul, W.; Battelle Memorial Institute, Pacific Northwest Division, Intellectual Property Services, P.O. Box 999, Richland, WA 99352 (US).		(81) Designated States: BR, CA, CN, JP, MX, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: PLASMA ENHANCED CHEMICAL DEPOSITION WITH LOW VAPOR PRESSURE COMPOUNDS



(57) Abstract

A plasma-enhanced chemical deposition system is disclosed. The system includes a chamber (106) with a substrate (104) at the bottom. A gas inlet (118) is at the top left, leading to a distribution manifold (120) with vertical tubes (128). A central vertical tube (122) is also shown. A gas outlet (130) is at the bottom left. A curved electrode (200) is on the right, with a gap (202) between it and the substrate. Arrows (2a) indicate gas flow from the inlet, through the manifold, and towards the substrate. A curved arrow (102) indicates the rotation of the substrate.

PLASMA ENHANCED CHEMICAL DEPOSITION
WITH LOW VAPOR PRESSURE COMPOUNDS

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FIELD OF THE INVENTION

The present invention relates generally to a method of making plasma polymerized films. More specifically, the present invention relates to making a plasma polymerized film via plasma enhanced chemical deposition with a flash evaporated feed source of a low vapor pressure compound. As used herein, the term "(meth)acrylic" is defined as "acrylic or methacrylic". As used herein, the term "cryocondense" and forms thereof refers to the physical phenomenon of a phase change from a gas phase to a liquid phase upon the gas contacting a surface having a temperature lower than a dew point of the gas.

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BACKGROUND OF THE INVENTION

The basic process of plasma enhanced chemical vapor deposition (PECVD) is described in THIN FILM PROCESSES, J.L. Vossen, W. Kern, editors, Academic Press, 1978, Part IV, Chapter IV - 1 Plasma Deposition of Inorganic Compounds, Chapter IV - 2 Glow Discharge Polymerization, herein incorporated by reference. Briefly, a glow discharge plasma is generated on an electrode that may be smooth or have pointed projections. Traditionally, a gas inlet introduces high vapor pressure monomeric gases into the plasma region wherein radicals are formed so that upon subsequent collisions with the substrate, some of the radicals in the monomers chemically bond or cross link (cure) on the substrate. The high vapor pressure monomeric gases include gases of CH_4 , SiH_4 , C_2H_6 , C_2H_2 , or gases generated from high vapor pressure liquid, for example styrene (10 torr at 87.4 °F (30.8 °C)), hexane

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requires two sequential steps, cryocondensation followed by curing or cross linking, that are both spatially and temporally separate.

According to the state of the art of making plasma polymerized films, PECVD and flash evaporation or glow discharge plasma deposition and flash evaporation have not been used in combination. However, plasma treatment of a substrate using glow discharge plasma generator with inorganic compounds has been used in combination with flash evaporation under a low pressure (vacuum) atmosphere as reported in J.D. Affinito, M.E. Gross, C.A.. Coronado, and P.M. Martin, "Vacuum Deposition Of Polymer Electrolytes On Flexible Substrates." Paper for Plenary talk in "Proceedings of the Ninth International Conference on Vacuum Web Coating", November 1995 ed R. Bakish, Bakish Press 1995, pg 20-36., and as shown in FIG. 1. In that system, the plasma generator 100 is used to etch the surface 102 of a moving substrate 104 in preparation to receive the monomeric gaseous output from the flash evaporation 106 that cryocondenses on the etched surface 102 and is then passed by a first curing station (not shown), for example electron beam or ultra-violet radiation, to initiate cross linking and curing. The plasma generator 100 has a housing 108 with a gas inlet 110. ~~The gas may be oxygen, nitrogen, water or an~~ inert gas, for example argon, or combinations thereof. Internally, an electrode 112 that is smooth or having one or more pointed projections 114 produces a glow discharge and makes a plasma with the gas which etches the surface 102. The flash evaporator 106 has a housing 116, with a monomer inlet 118 and an atomizing nozzle 120, for example an ultrasonic atomizer. Flow through the nozzle

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(c) the substrate is proximate the glow discharge plasma for receiving and cryocondensing the glow discharge plasma thereon. All components are preferably within a low pressure (vacuum) chamber.

5 The method of the present invention has the steps of (a) flash evaporating a liquid monomer an evaporate outlet forming an evaporate; (b) passing the evaporate to a glow discharge electrode creating a glow discharge monomer plasma from the evaporate; and
10 (c) cryocondensing the glow discharge monomer plasma on a substrate and crosslinking the glow discharge plasma thereon, wherein the crosslinking results from radicals created in the glow discharge plasma and achieves self curing.

15 It is an object of the present invention to provide an apparatus and method combining flash evaporation with glow discharge plasma deposition.

 It is an object of the present invention to provide an apparatus and method of making a self curing polymer
20 layer.

 It is another object of the present invention to provide an apparatus and method of making a self curing PML polymer layer.

 It is another object of the present invention to
25 provide an apparatus and method of PECVD deposition of low vapor pressure monomer.

 An advantage of the present invention is that it is insensitive to a direction of motion of the substrate because the deposited monomer layer is self curing. In
30 the prior art, the deposited monomer layer required a radiation curing apparatus so that the motion of the substrate had to be from the place of deposition toward the radiation apparatus. Another advantage of the present invention is that multiple layers of materials
35 may be combined. For example, as recited in U.S. patents

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120 is atomized into particles or droplets 122 which strike the heated surface 124 whereupon the particles or droplets 122 are flash evaporated into a gas or evaporate that flows past a series of baffles 126 to an evaporate outlet 128 and cryocondenses on the surface 102. Cryocondensation on the baffles 126 and other internal surfaces is prevented by heating the baffles 126 and other surfaces to a temperature in excess of a cryocondensation temperature or dew point of the evaporate. Although other gas flow distribution arrangements have been used, it has been found that the baffles 126 provide adequate gas flow distribution or uniformity while permitting ease of scaling up to large surfaces 102. The evaporate outlet 128 directs gas toward a glow discharge electrode 204 creating a glow discharge plasma from the evaporate. In the embodiment shown in FIG. 2, the glow discharge electrode 204 is placed in a glow discharge housing 200 having an evaporate inlet 202 proximate the evaporate outlet 128. In this embodiment, the glow discharge housing 200 and the glow discharge electrode 204 are maintained at a temperature above a dew point of the evaporate. The glow discharge plasma exits the glow discharge housing 200 and cryocondenses on the surface 102 of the substrate 104.

It is preferred that the substrate 104 is kept at a temperature below a dew point of the evaporate, preferably ambient temperature or cooled below ambient temperature to enhance the cryocondensation rate. In this embodiment, the substrate 104 is moving and may be non-electrically conductive, electrically conductive, or electrically biased with an impressed voltage to draw the evaporate to the substrate 104.

Another embodiment of the invention is shown in FIG. 3. In this embodiment, the glow discharge plasma is directed toward the substrate 104.

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point to allow cryocondensation of the glow discharge plasma on the part 300 and thereby coat the part 300 with the monomer condensate and self cure into a polymer layer. Sufficiently proximate may be connected to, resting upon, in direct contact with, or separated by a gap or distance that permits the plasma to impinge upon the substrate. This distance that the plasma extends from the electrode will depend on the evaporate species, electrode 204/substrate 104 geometry, electrical voltage and frequency, and pressure in the standard way as described in ELECTRICAL DISCHARGES IN GASSES, F.M. Penning, Gordon and Breach Science Publishers, 1965, hereby incorporated by reference. The substrate 300 may be stationary or moving during cryocondensation. Moving includes rotation and translation and may be employed for controlling the thickness and uniformity of the monomer layer cryocondensed thereon. Because the cryocondensation occurs rapidly, within milli-seconds to seconds, the part may be removed after coating and before it exceeds a coating temperature limit.

In operation, either as a method for plasma enhanced chemical vapor deposition of low vapor pressure monomeric materials onto a substrate, or as a method for making self-curing polymer layers (especially PML), the method of the invention has the steps of (a) flash evaporating a liquid monomer an evaporate outlet forming an evaporate; (b) passing the evaporate to a glow discharge electrode creating a glow discharge monomer plasma from the evaporate; and (c) cryocondensing the glow discharge monomer plasma on a substrate and crosslinking the glow discharge plasma thereon. The crosslinking results from radicals created in the glow discharge plasma thereby permitting self curing.

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evaporator 106 through a gas inlet 130 upstream of the evaporate outlet 128, preferably between the heated surface 124 and the first baffle 126 nearest the heated surface 124. Additional gases may be organic or
5 inorganic for purposes included but not limited to ballast, reaction and combinations thereof. Ballast refers to providing sufficient molecules to keep the plasma lit in circumstances of low evaporate flow rate. Reaction refers to chemical reaction to form a compound
10 different from the evaporate. Ballast gases include but are not limited to group VIII of the periodic table, hydrogen, oxygen, nitrogen, chlorine, bromine, polyatomic gases including for example carbon dioxide, carbon monoxide, water vapor, and combinations thereof. An
15 exemplary reaction is by addition of oxygen gas to the monomer evaporate hexamethyldisiloxane to obtain silicon dioxide.

Example 1

20 An experiment was conducted to demonstrate the present invention as shown in FIG. 2 and described above. Tetraethyleneglycoldiacrylate was used as the liquid monomer. The heated surface was set at a temperature of about 650 °F (343 °C). Liquid monomer was introduced to
25 the inlet via a capillary with 0.032 inch I.D. The ultrasonic atomizer had a tip with 0.051 inch I.D. Rate of deposition of the polymer layer was 0.5 m/min for 25 micron thick polymer layer and 100 m/min for 1 micron thick polymer layer. Visual inspection of the cured
30 polymer layer did not reveal any pin holes or other flaw.

CLOSEUP

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I claim:

1. An apparatus in a vacuum chamber for plasma enhanced chemical vapor deposition of low vapor pressure monomeric materials onto a substrate, comprising:

(a) a flash evaporation housing with a monomer atomizer for making monomer particles, heated evaporation surface for making an evaporate from said monomer particles, and an evaporate outlet; and

(b) a glow discharge electrode downstream of the evaporate outlet creating a glow discharge plasma from the evaporate; and

(c) said substrate receiving and cryocondensing said glow discharge plasma thereon.

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2. The apparatus as recited in claim 1, wherein the substrate is proximate the glow discharge electrode and is electrically biased with an impressed voltage.

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3. The apparatus as recited in claim 1, wherein said glow discharge electrode is positioned within a glow discharge housing having an evaporate inlet proximate the evaporate outlet, said glow discharge housing and said glow discharge electrode maintained at a temperature

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4. The apparatus as recited in claim 1, wherein said flash evaporation housing has opposing baffles placed between a heated surface and the evaporate outlet.

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5. The apparatus as recited in claim 1, further comprising a gas inlet upstream of said evaporate outlet.

6. A method for plasma enhanced chemical vapor deposition of low vapor pressure monomeric materials onto

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10. The method as recited in claim 9, wherein said acrylic monomer is selected from the group consisting of tripropyleneglycol diacrylate, tetraethylene glycol diacrylate, tripropylene glycol monoacrylate,
5 caprolactone acrylate, and combinations thereof;

11. The method as recited in claim 6, wherein said substrate is cooled.

10 12. The method as recited in claim 6, further comprising adding an additional gas.

13. The method as recited in claim 12, wherein said additional gas is a ballast gas.

15 14. The method as recited in claim 12, wherein said gas is a reaction gas.

20 15. The method as recited in claim 14, wherein said reaction gas is oxygen gas and said evaporate includes hexamethyldisiloxane.

16. An apparatus for making self-curing polymer layers in a vacuum chamber, comprising:

25 (a) a flash evaporation housing with a monomer inlet, monomer atomizer for receiving a liquid monomer from said monomer inlet and making monomer particles, a heated evaporation surface for making an evaporate from said monomer particles, and an evaporate
30 outlet; and

(b) a glow discharge electrode downstream of the evaporate outlet creating a glow discharge plasma

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22. The method as recited in claim 21, wherein the substrate is proximate the glow discharge electrode and is electrically biased with an impressed voltage, receiving the monomer plasma cryocondensing thereon.

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23. The method as recited in claim 21, wherein said glow discharge electrode is positioned within a glow discharge housing having an evaporate inlet proximate the evaporate outlet, said glow discharge housing and said glow discharge electrode maintained at a temperature above a dew point of said evaporate and said substrate is downstream of said monomer plasma, substantially not biased with an impressed voltage, receiving the monomer plasma cryocondensing thereon.

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24. The method as recited in claim 21, wherein said monomer is selected from the group consisting of acrylic monomer, methacrylic monomer and combinations thereof.

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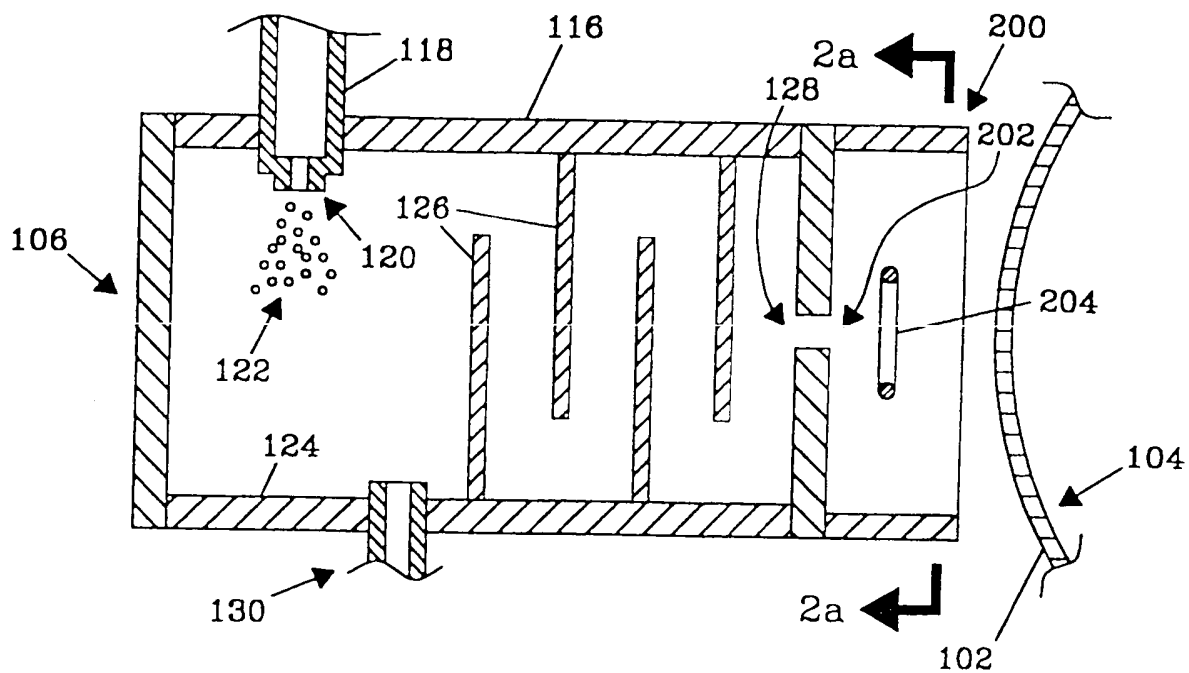
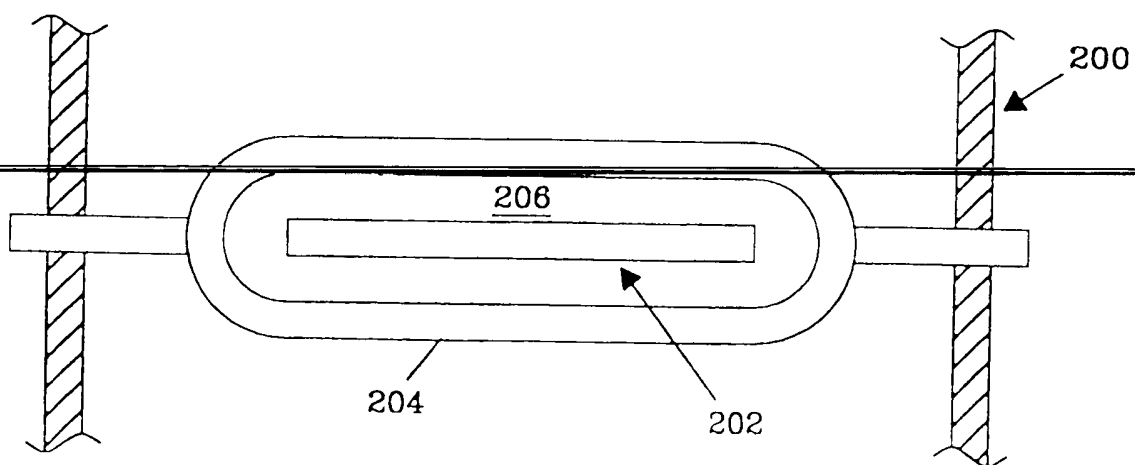
25. The method as recited in claim 24, wherein said acrylic monomer is selected from the group consisting of tripropyleneglycol diacrylate, tetraethylene glycol diacrylate, tripropylene glycol monoacrylate, caprolactone acrylate, and combinations thereof;

26. The method as recited in claim 21, wherein said substrate is cooled.

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27. The method as recited in claim 21, wherein said low vapor pressure is less than about 10 torr at 83 °F (28.3 °C).

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*Fig. 2*

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 98/20741

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C16/44 C23C16/50 B05D7/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C23C B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AFFINITO J D ET AL: "HIGH RATE VACUUM DEPOSITION OF POLYMER ELECTROLYTES" JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY: PART A, vol. 14, no. 3, PART 01, May 1996, pages 733-738, XP000620547 see the whole document ---	1,16,21
A	US 5 032 461 A (SHAW DAVID G ET AL) 16 July 1991 see column 8, line 24 - column 13, line 10; figures 2,2A,5 ---	1,16,21
A	US 5 620 524 A (FAN CHIKO ET AL) 15 April 1997 see column 5, line 7 - line 10 see column 11, line 54 - column 13, line 20; figure 1 --- -/--	1,16,21

☒ Further documents are listed in the continuation of box C

☒ Patent family members are listed in annex

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 340-2040, Tx: 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Patterson, A

INTERNATIONAL SEARCH REPORT

information on patent family members

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